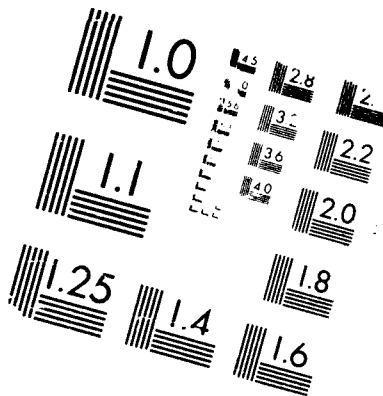


AD-A194 585 NEW SYNTHETIC APPROACHES TO TAT(U) BONN UNIV (GERMANY F 1/1  
R) H WANNHOFF 27 AUG 86 DAJA45-85-C-0016

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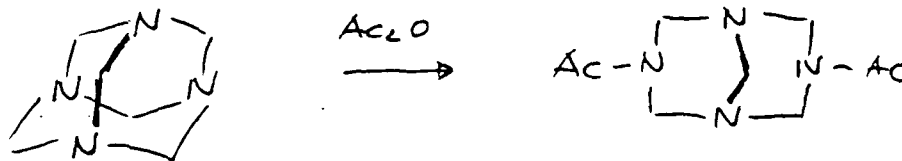
Ref.: Contract No. DAJA 45-85-C-0016  
"New Synthetic Approaches to TAT"

FOURTH INTERIM REPORT (Item 0004)

On the basis of my recent visit (July 21, 1986) to US-Army Armament, Munitions and Chemical Command, Picatinny Areal, Dover, NJ, and the conference held there with Dr. Everett E. Gilbert and his group, besides the current work described in our FIRST - THIRD Interim Report (Items 0001 - 0003), and with regard to the Brief Travel Report (Dated July 29, 1986), some novel and promising routes to TAT are pursued at the moment.

1) Report on the work of Mr. Marcus Bonden

Besides the study of partial destruction of urotropine (hexamethylenetetramine) itself, more interest is cast now on the 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane ("DAPT"), which is easily accessible from urotropine by partial acetolysis, according to V.I. Siele, M. Warman, and E.E. Gilbert, J. Heterocycl. Chem. 11, 237 (1974):

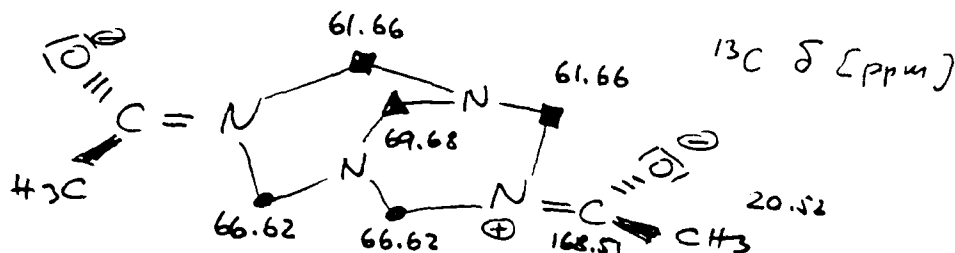


This experiment was easily repeated (lit.-mp 195°C; found mp 206°C). In order to get deeper insights into the chemical properties of this important pre-stage for TAT, the spectroscopic properties have been inspected. The high-resolution MS gave the exact and consistent molecular ion  $m/z$  212.1271 along with  $C_9H_{14}N_4O_2$ . The  $^1H$  and  $^{13}C$  NMR spectra offer a complex scheme pointing to a molecule of the following structure and involving an amide resonance form which causes a definite aniso-

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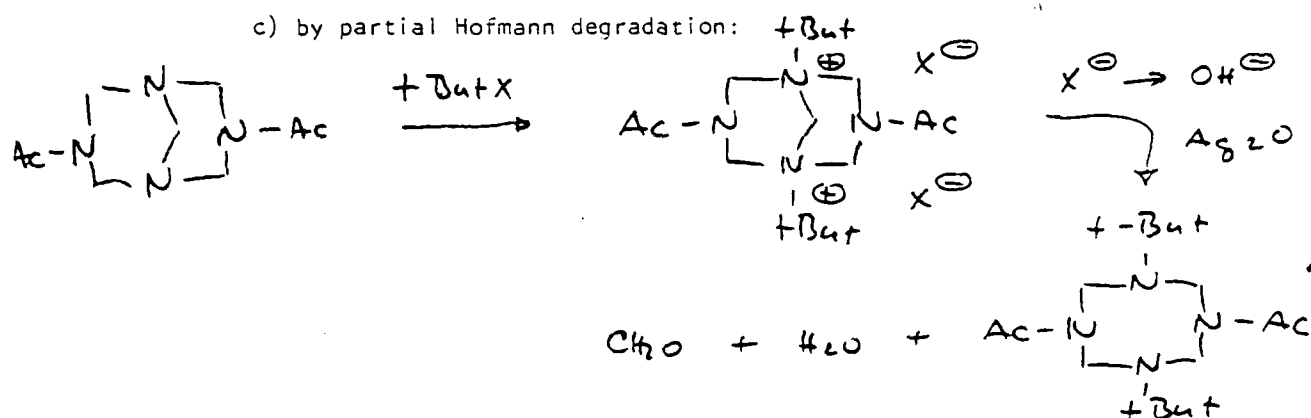
chronism for the adjacent CH<sub>2</sub>-groups (syn/anti shifts):



The <sup>1</sup>H NMR shows accordingly two singlets at δ 2.07 and 4.23 for the acetyl group, a pseudo-singlet for the bridging methylene, as well as two AB-systems at δ 5.00 (J = 14 and 132 Hz) and 4.81 (J = 14 Hz, W-coupling J = 2 Hz). A further investigation involving a 2D-CH-two dimensional <sup>1</sup>H/<sup>13</sup>C NMR spectrum is just carried out.

This DAPT is now further investigated with the aim to remove selectively the remaining >N-CH<sub>2</sub>-N< bridge by means of the reagents mentioned already in the previous interim reports 1-3:

- electrooxidative way (cyclic voltammetry is under investigation)
- by mild and selective oxidative reagents, such as Cu<sup>2+</sup>, K<sub>3</sub>[Fe(CN)<sub>6</sub>], X<sub>2</sub>PPh<sub>3</sub>, POX<sub>3</sub>, TMS, NCS etc.
- by partial Hofmann degradation:

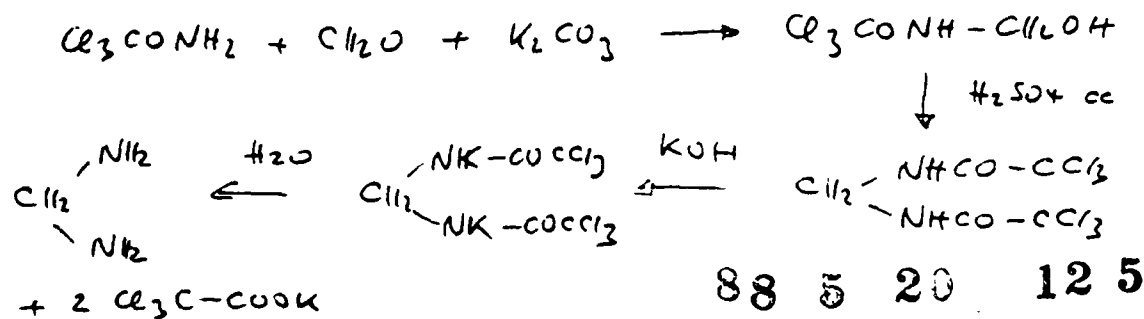


Thus, a mixed substituted (Ac, tBut) tetrazocane is expected to result, where the substituents are easily exchangeable.

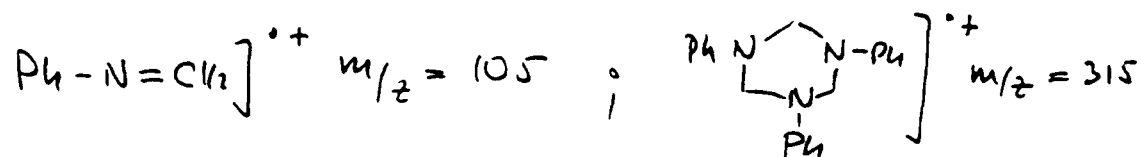
#### Search of suitable building units for TAT

In addition to the experiments described previously, we want to follow a classical procedure by A. Einhorn and T. Mauermayer, Liebigs Ann.Chem. 343, 306 ff. (1905).

In this communication a simple approach to methylenediamine is given:

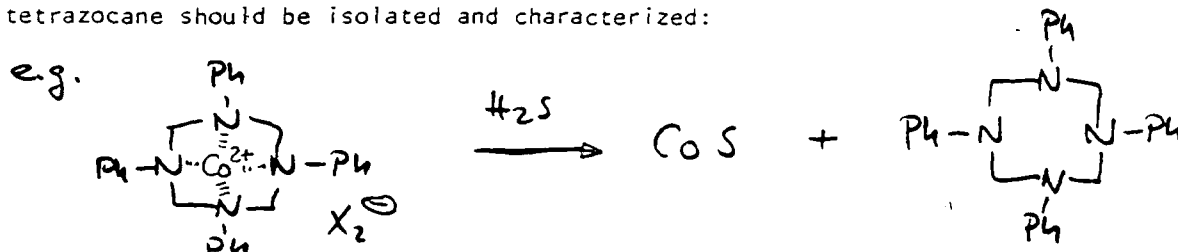


under the conditions of electron impact methylenedianiline is fragmented and a hexahydro-triazine ion is formed; both species form peaks of high intensity:



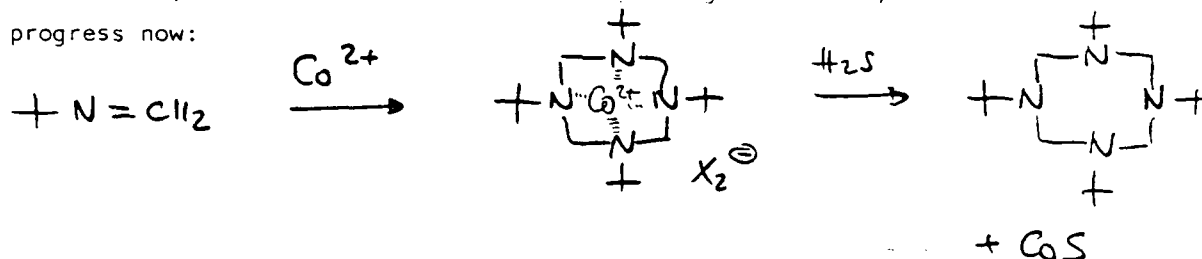
Therefore, it can be concluded that 8-membered  $\text{Co}^{2+}$ -tetrazocane complex has been formed (no pertinent analytical data were available from the Roumanian paper!). Supplementary, informations are expected from a single-crystal X-ray analysis, which is planned for the near future, as soon as suitable single crystals are available.

Consequently, chemical destruction of this complex is under progress, now; by treatment with  $\text{H}_2\text{S}$ ,  $\text{CN}^-$ , EDTA,  $\text{CO}_2$ , the central atom  $\text{Co}^{2+}$  should be removed, and free tetrazocane should be isolated and characterized:

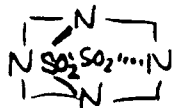


According to the results of the Conference of July 21, 1986 in Picatinny Areal mentioned above, it is planned to extend the Roumanian synthesis also to larger ring compounds, such as hexaazacyclododecane, dodekaazacyclotetraeicosane, which are of similar high interest like TAT.

Furthermore, tetramerization of the corresponding t-But-methyleneimine is under progress now:



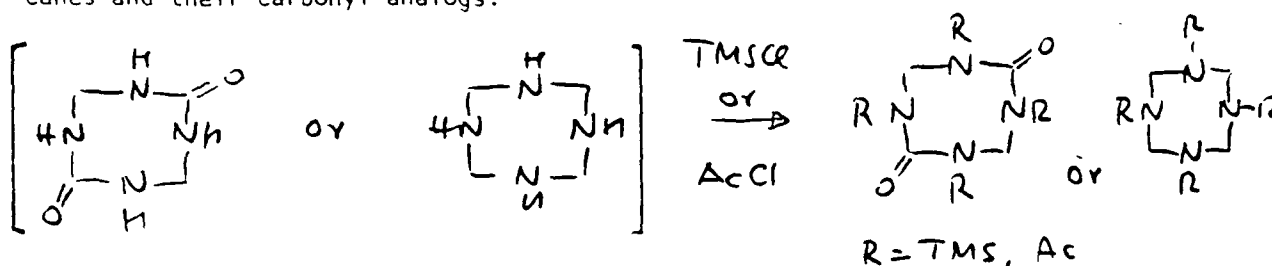
Finally, a suggestion stemming from the conference at Picatinny Areal to start work also on tetramethylenedisulfotetramine (Hecht & Hennecke, Angew.Chem. 61, 365 (1949):



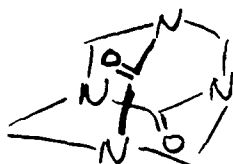
is considered now carefully, but with some restrictions, as this compound exhibits violent convulsant activities. Photochemical extrusion reaction of  $\text{SO}_2$ -bridges might offer another successful approach to TAT.

Heinrich Wamhoff  
Professor Dr. Heinrich Wamhoff

The elusive methylenediamine resulting from this sequence should be reacted in situ with functional C-1-components, like formaldehyde, phosgene, dialkyl carbonates, orthoformic esters, and Staab's reagent (Carbonyl bisimidazole) for creating tetrazocanes and their carbonyl analogs:



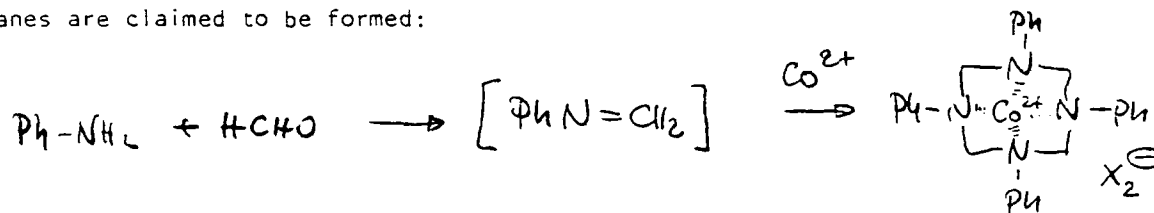
Furthermore, the reaction of urea with formaldehyde is strongly suggested. In a 2:1-manner the formation of an urotropine molecule with two carbonyl bridges, such as:



might be expected, whose selective destruction ( $n \rightarrow \pi^*$ -excitation of the  $\text{C}=\text{O}$  chromophores and subsequent  $\alpha$ -cleavage) is planned.

## 2) Report on the work of Mr. Johannes Nagelschmitz

In the meantime, Mr. Nagelschmitz has repeated the work of the Roumanian group (M. Brezeanu, D.N. Marinescu-Stefanescu, *Analele Universitatii Bucuresti Chimii* 1973, 22 (1) 21; Chem.Abstr. 81, 98800 f (1974)). By reacting aniline and formaldehyde in DMF or DMSO and by template effect of metal ions, like  $\text{Co}^{2+}$ , tetrazocanes are claimed to be formed:



A broad CA-on line recherche has revealed and made sure that no further or forthcoming paper has appeared since 1973.

As we have found running this procedure, there is formed in fact a green solid metal complex. This product has been intensively studied, e.g. by high-field MS, and in fact a molecular ion has been found at  $m/z$  420.2101, which points unambiguously to an elemental composition  $\text{C}_{28}\text{H}_{27}\text{N}_4$  (420 i.e.  $\text{M}^+-1$ ); this behaviour supports strongly that the  $\text{Co}^{2+}$ -tetrazocane complex is - as expected earlier by us - a weak complex, so that under the conditions of MS measurement ( $10^{-6}$  Torr,  $230^\circ\text{C}$ ,  $70\text{eV}$ ) considerable amounts of the tetrazocane ligand are sufficient volatile.

Accordingly, the fragmentation pattern supports the structure of the complex, as

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